Hydride Olefin complexes of tantalum and niobium

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SUMMARY

This thesis describes investigations on low-valent tantalum and niobium hydride and alkyl complexes, particularly the dicyclopentadienyl tantalum hydride olefin complexes $Cp_2Ta(H)L$ (L = olefin). These compounds, which are postulated in the hydrogenation of olefins catalyzed by Cp_2TaH_3, are readily prepared in high yields *via* the reaction of Cp_2TaCl_2 with alkyl Grignards RMgX. With unsymmetrically substituted olefins two isomers are possible, depending on the orientation of these substituents relative to the hydride ligand. The Grignard reaction presents an excellent possibility to prepare these isomers separately.

Much attention is paid to the reversible β-H addition-elimination process, according to equilibrium (1).

$$Cp_2Ta(H)C_nH_{2n} \rightleftharpoons Cp_2TaC_nH_{2n+1} \qquad (1)$$

Apart from a general introduction, which deals with some aspects of the catalytic hydrogenation of olefins, predictions on the position of equilibrium (1), based on theoretical considerations, are made.

Chapter II describes the synthesis of hydride olefin complexes of tantalum and niobium, from Cp_2MCl_2 and Grignards RMgX. The last step of the reaction probably proceeds *via* a stereospecific β-H elimination of the monoalkyl species $Cp_2MC_nH_{2n+1}$ to give $Cp_2M(H)C_nH_{2n}$. Decomposition of n-alkyl products initially leads to *endo* $Cp_2M(H)C_nH_{2n}$ complexes exclusively, whereas iso-alkyls predominantly give *exo* $Cp_2M(H)C_nH_{2n}$ complexes. The hydride olefin complexes are thermally remarkably stable, probably as a consequence of a strong interaction between the Cp_2MH fragment and the olefin (IR, ^{13}C NMR).

In reactions of hydride olefin complexes with electron donors, *e.g.* PEt_3, the olefin is replaced by the phosphine ligand. On the other hand, with π-acceptor ligands L we expect the formation of alkyl compounds.

Indeed, *endo* hydride olefin complexes are converted into mono n-alkyl compounds $Cp_2MR.L$ in the reactions with unsaturated substrates such as carbon monoxide (Chapter III), isocyanides (Chapter IV), cyclooctatetraene (Chapter V), organ
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(Chapter V), organic cyanides and carbon disulfide (Chapter VI). Both "end-on" (L = CO, R'NC) and dihapto (L = C_8H_8, R'CN) coordination of L are found in the complexes $Cp_2MR.L$.

The monoalkyl adducts are all thermally very stable; in these complexes a strong back donation from the metal to the π-acceptor ligand is observed.

The crystal structure of $Cp_2TaC_3H_7.C_8H_8$ (Chapter V) shows a dihapto coordinated C_8H_8 ligand; remarkably enough, the carbon skeleton of this ligand is planar.

Despite the high thermal stability of the alkyl adducts, the dihapto coordinated ligands partly dissociate in solution to give only the original (*endo*) hydride olefin complexes, illustrating the reversibility of the β-H addition-elimination process.

The *exo* hydride olefin complexes are less reactive. Reactions were observed only with CO (substitution of the olefin) and CS_2 (insertion of the olefin into the M-H bond, yielding an iso-alkyl adduct of CS_2).

The niobium hydride olefin complexes are much more reactive than the corresponding tantalum derivatives, but reactions of both tantalum and niobium complexes proceed in a similar way. For the study of the β-H addition-elimination equilibrium the tantalum compounds are favoured due to their higher thermal stability. In addition, the synthesis of *endo* and *exo* hydride olefin complexes, respectively, is more selective for tantalum.

In Chapter VII a detailed description is given of the experiments performed.